ANALYSIS OF THE MINERAL MONAZITE FOR RARE-EARTHS AND ASSOCIATED METALS

A Thesis

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by

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DEDICATION

To my wife Jane and daughter Lisa

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CHAPTER I

THE PROBLEM AND ITS IMPORTANCE

I. INTRODUCTION

Monazite (Ce, La, Y, Th) PO_4, a mineral widely distributed in nature with large deposits found in Brazil, Ceylon, Norway, India, Australia, South Africa and the United States, is one of the most important sources of thorium and the rare-earth elements. The mineral is a thorium--rare-earth phosphate. The thorium content varies from 4% to 30%, with most ores containing about 8% thorium. Varying amounts of other elements, such as silicon, calcium, magnesium, iron, beryllium, aluminium, titanium, zirconium, uranium and lead are present. Monazite belongs to the monoclinic crystal system and its color ranges from yellowish or reddish brown to brown (1).

II. THE PROBLEM

It was the purpose of this study (1) to investigate the physical and chemical properties of the rare-earth elements and associated rare-earth elements present in the monazite sample; (2) to separate the rare-earth elements and associated metals from all other elements present in the monazite sample; (3) to determine quantitatively the amount of rare-earth elements and associated

rare-earth elements present in the monazite sample.

III. IMPORTANCE OF THE STUDY

For years the rare-earth elements were restricted to limited use. For the most part, the rare-earth metals were used in five primary areas; arc carbons, flints for lighters, glass polishing, cracking catalysts and non-dularizing agents for iron. For these uses pure rare-earth elements were not needed, as mixtures could do the job equally as well at a far lower cost.

Presently, the electronics industry has created a demand for pure rare-earth elements. This demand was created by the advent of color television. Color television depends on three phosphors: red, green and blue. The rare-earth metals are used in a new red phosphor which is superior to all previously tried red phosphors, which were found to be too dull. This new red phosphor is a europium-activated yttrium vanadate type with different companies using slight variations in this system. Thousands of pounds of pure europium oxide and pure yttrium oxide will be needed in the near future and many sources both domestic and foreign will have to be exploited.

For new uses the industry which holds the most hope for rare-earth metal consumption is the electronics industry. Many of the rare-earth metals are finding use as solid-state microwave devices which are widely used in radar

systems and in communications systems. Rare-earth metals are also being considered for use with new laser systems which are currently being developed (2).

With the demand for rare-earth elements and associated metals continually increasing, it is of the utmost importance, therefore, to analyze all monazite deposits for ore content.

CHAPTER II

REVIEW OF THE LITERATURE

Many articles have been written concerning the physical and chemical properties of the rare-earth elements (3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13). Literature is also available concerning the physical and chemical properties of the mineral monazite (1, 9, 14). Recently much work has been done to separate rare-earth mixtures by using spectrophotometric techniques (4, 5, 15, 16) and a scheme for the complete analysis of the mineral monazite has also been published (14).

THE CHEMICAL AND PHYSICAL PROPERTIES OF THE RARE-EARTH ELEMENTS

The rare-earth elements are not at all rare, these elements constitute the largest naturally occuring group of elements in the periodic system. It is because of the similarity in chemical and physical properties which cause several of the rare-earth elements to be found together in many minerals. It is because of this similarity in chemical and physical properties which causes the difficulty in trying to isolate the rare-earth elements from one another (8).

The rare-earth elements range from element number

58 to element number 71 in the periodic system. These elements include Cerium, Praseodymium, Neodymium, Promethium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium and Lutetium. Yttrium and Lanthanum are always found with the rare-earth elements in the more important rare-earth minerals (1).

The rare-earth elements are also known as the inner transition elements. In the rare-earth elements the distinguishing electrons occupy the 4f level.

TABLE I

THE ELECTRONIC CONFIGURATION OF THE RARE-EARTH ELEMENTS

Element	At. No.	Electronic Configuration
*Y	39	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^1 5s^2$
*La	57	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^1 6s^2$
**Ce	58	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^1 5s^2 5p^6 5d^1 6s^2$
Pr	59	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^3 5s^2 5p^6 6s^2$
Nd	60	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^4 5s^2 5p^6 6s^2$
Pm	61	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^5 5s^2 5p^6 6s^2$
Sm	62	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^6 5s^2 5p^6 6s^2$
Eu	63	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^7 5s^2 5p^6 6s^2$

* Lanthanum and yttrium are included because of their association and similarity with the other rare-earth elements.

** The configurations of cerium and terbium are still uncertain.

TABLE I

THE ELECTRONIC CONFIGURATION OF
THE RARE-EARTH ELEMENTS

Element	At. No.	Electronic Configuration
Gd	64	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^7 5s^2 5p^6 5d^1 6s^2$
**Tb	65	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^9 5s^2 5p^6 6s^2$
Dy	66	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{10} 5s^2 5p^6 6s^2$
Ho	67	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{11} 5s^2 5p^6 6s^2$
Er	68	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{12} 5s^2 5p^6 6s^2$
Tm	69	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{13} 5s^2 5p^6 6s^2$
Yb	70	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 6s^2$
Lu	71	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 6s^2$

** The configurations of cerium and terbium are still uncertain.

Due to the fact that electrons are added to a well-shielded lower orbital, gives the rare-earth elements a number of unusual properties. These properties include similarity of oxidation states, unusual light absorption spectra, and magnetic properties (6, 8, 9, 12).

The primary oxidation state of the rare-earth elements is +3, which is stable in aqueous media. Evidence obtained from spectrographic data indicates that the stabilities of lanthanum (III), gadolinium (III) and lutetium (III) can be related to the fact that the 4f orbitals are empty, half filled and completely filled. The common oxidation state of cerium (IV) is due to the fact that it is attaining the same stable configuration as lanthanum (III) which has an outermost configuration of $4f^{0}5s^{2}5p^{6}$. Praseodymium is also found to exist in a +4 oxidation state and in doing so it approaches the stable lanthanum (III) configuration but never actually achieves this stable configuration. For praseodymium to achieve the stable configuration of lanthanum (III) it must lose five electrons and praseodymium (V) has never been known to exist. The outermost electronic configuration of gadolinium (III), $4f^{7}5s^{2}5p^{6}$, is achieved by europium (II) and terbium (IV). This configuration is approached by samarium (III) which does not achieve this stable electronic configuration. The lutetium (III) outermost electronic configuration of $4f^{14}5s^{2}5p^{6}$ is achieved by ytterbium (II) (8).

TABLE II

THE KNOWN OXIDATION STATES OF
THE RARE-EARTH ELEMENTS

Symbol	At. No.	Oxidation State	Probable Electronic Configuration
La	57	+3	$4f^0$
Ce	58	+3, +4	$4f^1$, $4f^0$
Pr	59	+3, +4	$4f^2$, $4f^1$
Nd	60	+3	$4f^3$
Pm	61	+3	$4f^4$
Sm	62	+2, +3	$4f^6$, $4f^5$
Eu	63	+2, +3	$4f^7$, $4f^6$
Gd	64	+3	$4f^7$
Tb	65	+3, +4	$4f^8$, $4f^7$
Dy	66	+3	$4f^9$
Ho	67	+3	$4f^{10}$
Er	68	+3	$4f^{11}$
Tm	69	+3	$4f^{12}$
Yb	70	+2, +3	$4f^{14}$, $4f^{13}$
Lu	71	+3	$4f^{14}$

It is found that most of the rare-earth elements including lanthanum are strongly paramagnetic. This property is associated with unpaired electrons that are in the 4f shell and which make spin and orbital contributions to the magnetic moment.

In the series lanthanum--lutetium one finds a decrease in atomic size with an increase in atomic number. This is known as the Lanthanide Contraction and is due to the fact that the addition of electrons to the well-shielded 4f orbitals can not overcome the effect of increased nuclear charge. A similar effect is noted in the series lanthanum (III)--lutetium (III) (8).

METHODS USED FOR THE SEPARATION OF RARE-EARTH ELEMENTS

The methods for separating the rare-earth elements can be explained in terms of two broad catagories: classical methods and modern methods. Under modern methods are included ion-exchange separation and liquid-liquid extraction techniques. The classical methods can be grouped under three main categories: fractional crystallization, fractional precipitation and thermal reactions. There are several classical fractional crystallization separation methods. Lanthanum, praseodymium and neodymium may be separated by forming the double ammonium nitrate,

$R(NO_3)_2 \cdot 2NH_4NO_3 \cdot 4H_2O$. In addition, sulfates and double sulfates have been used. Many complex salts have been investigated, especially the ethylenediaminetetraacetic acid complex. The classical methods involving fractional precipitation methods are based on differences in basicity, formation of double salts, and changes in oxidation states. Classical thermal reactions have been used to separate rare-earth chlorides by volatilization. Most of these methods are time consuming, tedious and often lead to products which are not very pure. It was not until the modern methods of ion-exchange and liquid-liquid extraction that separations of the rare-earth elements have become feasible. Separation of the rare-earth elements by liquid-liquid extraction has been investigated since 1937. Since that time many different solvents have been used. Each solvent has its own particular characteristics and one is referred to the literature for further information (14). For analytical purposes it is necessary to turn toward ion-exchange separations of the rare-earth elements. It is through this method that components of a mixture may be resolved completely and the individual components may be recovered quantitatively in a high degree of purity. Ion-exchange techniques for separating a mixture is based on sorption of the ions on an exchange resin followed by differential displacement of the individual ions.

Much material has been published concerning various complexing agents and reagents. Many papers have also been published concerning the pH and temperatures versus column efficiency (17, 18, 19).

ANALYTICAL SPECTROSCOPY OF THE RARE-EARTH ELEMENTS

The spectra of the rare-earth elements is the most powerful property available for determining components of mixtures containing the rare-earth elements. There are four main techniques of analytical spectroscopy which have found general application. These techniques are optical absorption spectroscopy, optical fluorescence spectroscopy, optical emission spectroscopy and x-ray fluorescence spectroscopy (13).

In the investigation of the absorption spectra of aqueous solutions of the rare-earth elements, it is seen that there is absorption in the ultraviolet, visible and infrared regions of the spectrum. These absorption bands are complex and sharply defined. These sharp bands are due to the pure electronic transitions involving the 4f subshell which is protected from perturbations by ionic fields outside the atomic system by the 5p and 5s outer subshells. Yttrium, lanthanum and lutetium are the only elements in the rare-earth group which possess no absorption bands in the optical region of the spectrum. The major draw back to optical absorption spectroscopy is its inability to determine trace quantities of rare-earth impurities.

TABLE III

MOLAR ABSORPTIVITIES OF THE RARE-EARTH ELEMENTS FROM A BECKMAN MODEL D U SPECTROPHOTOMETER (4)

Rare-Earth	Wavelength ($m\mu$)	Slit Width (mm)	ϵ $\frac{1}{\text{mole-cm}}$	ϵ $\frac{1}{\text{mole-cm}}$ *
Nd	354.0	0.020		5.05
	521.6	0.020	4.29	4.29
	575.5	0.020	6.93	6.93
	739.5	0.020	7.03	
	794.0	0.020	9.96	
Pr	444.2	0.020	10.31	10.31
Sm	401.5	0.035	3.23	3.31
Eu	394.2	0.045	2.91	3.01
Gd	272.8	0.020		3.35
Dy	350.4	0.020		2.52
	365.0	0.020		2.05
	908.0	0.020	2.38	
Ho	287.0	0.020		3.31
	361.1	0.020		2.18
	450.8	0.020	4.00	4.00
	537.0	0.020	4.58	4.58
	690.4	0.020	3.05	3.05
Er	379.6	0.055	6.57	6.93
	523.5	0.020	3.20	3.20
Tm	683.0	0.030	2.56	
Yb	908.0	0.020	1.97	

* extinction coefficient determined using a photomultiplier

Although optical fluorescence spectroscopy of the rare-earth elements has been known since the 1930's, analytical applications have not been too extensive. The main reason for this slow development is due to the weak fluorescence lines which are obtained and that the best wavelength for exciting the fluorescence is below 2500A (13).

Optical emission spectroscopy can be utilized for the detection and quantitative determination of all rare-earth elements. The biggest difficulty encountered in optical emission spectroscopy is that many of the spectra are very complex, possessing thousands of lines of uniform intensity. Because of this, optical emission spectroscopy is usually only used to determine those elements which cannot be determined by optical absorption spectroscopy (13).

TABLE IV

EMISSION LINES AND LIMITS OF DETECTABILITY
FOR LANTHANUM AND YTTRIUM USING THE
BECKMAN MODEL D U SPECTROPHOTOMETER (20)

Element	Wavelength (mμ)	Ultimate Detection Limit
Lanthanum	442	0.5 ppm
	438	0.5 ppm
	560	0.6 ppm
Yttrium	444	5.0 ppm
	483	5.0 ppm

The last method which is commonly utilized is x-ray fluorescent spectroscopy. This technique is based on the intensity measurement of the fluorescent x-rays emitted when a sample is irradiated with energetic x-rays. The major draw back in this method is due to line interferences and overlap of absorption edges.

CHAPTER III

THE EXPERIMENTAL INVESTIGATION OF THE MONAZITE FOR RARE-EARTH ELEMENTS AND RELATED METALS

RECOVERY AND PREPARATION OF THE MONAZITE

The sample of monazite was obtained by Dr. James Edwin Johnson from the Mars Hill section of Madison County, North Carolina. The sample weighed approximately 200 grams and was yellowish-brown in color. A piece of the sample was chipped off and placed in a Diamonite morter, a synthetic sapphire molded under very high pressure and temperature. The sample, which was found to be extremely hard, was ground to a fine powder using a Diamonite pestle.

THE OPENING OF THE MONAZITE

Of all the methods which can be used for the decomposition of the monazite, the method involving the use of concentrated sulphuric acid seems to be the best. The soluble fraction of the sulphuric acid digest may contain any or all of the rare-earth metals with lanthanum, yttrium, aluminium, calcium, magnesium, iron lead, titanium, uranium, manganese, sodium and potassium.

The insoluble residue from the monazite digestion is generally of a complex composition. It may contain several oxide minerals, such as quartz, magnetite, rutile and ilmenite, with several other silicate minerals (14).

SULPHURIC ACID ATTACK ON THE MONAZITE

Six samples, of about 1.0 grams of the finely powdered monazite were accurately weighed using a Mettler Gram-Atic balance. The weighed samples were then carefully transferred to a 15 ml platinum crucible.

TABLE V

THE WEIGHTS OF THE INDIVIDUAL SAMPLES OF MONAZITE TAKEN FOR ANALYSIS

Sample #	Weight Of Sample
1	1.3282 g
2	1.2420 g
3	1.5021 g
4	1.1688 g
5	1.1390 g
6	1.3281 g

To each sample 10 ml of reagent grade concentrated sulphuric acid was added. The crucible was then covered and placed on a type 2200 Thermolyne hot plate with the temperature regulated to 250°C. The sulphuric acid attack was allowed to continue until the digestion was complete. The time for complete digestion varies with the size of the sample, however it was found that the digestion is usually complete in forty to sixty hours. After the sample was given sufficient time to cool, its contents were quantitatively transferred to a 250 ml beaker containing 100 ml of distilled water, using a jet of distilled water to complete the transfer. The beaker was then gently warmed on a hot plate for 15 minutes or until the solution was clear. A small amount of macerated Whatman No. 42 ashless filter paper was added and the solution was stirred for five minutes. The solution was again allowed to cool. Sufficient time, approximately 1 hour, was given to allow the macerated filter paper to settle. The solution was then filtered through 8.5 cm Whatman No. 42 filter paper using gentle suction. At this point there should be absolutely no residue left in the filtrate. The filter paper was then washed with 100 ml of distilled water. The washings and the filtrate were then combined and the solution was diluted to 400 ml. This solution was then saved and used for the quantitative determination of the acid-soluble metals.

THE DETERMINATION OF THE ACID INSOLUBLE RESIDUE

The filter paper containing the acid insoluble residue was placed in a weighed platinum crucible. The crucible was covered and gently heated using a bunsen burner. After most of the paper had charred, the crucible was placed in a type 56 Multiple Unit heavy duty furnace. The temperature was regulated to 1000°C to remove all carbonaceous material. The entire process was usually complete within two hours. The crucible was then removed and placed in a desiccator with Drierite (anhydrous $CaSO_4$) as the desiccant, and allowed to cool to room temperature. The insoluble residue was then weighed to constant weight using the Gram-Atic balance. Two determinations were made.

TABLE VI

DETERMINATION OF THE ACID INSOLUBLE RESIDUE

Sample #	Weight Of Sample	Weight Of Residue	% Residue
5	1.1390 g	0.1059 g	8.42%
6	1.3281 g	0.1127 g	8.41%

THE DETERMINATION OF THE WATER CONTENT IN THE MONAZITE

Two samples of finely ground monazite were weighed using the Gram-Atic balance and placed in platinum crucibles. The samples were then put into a Fisher Senior Isotemp oven and allowed to remain at 110°C for several hours. The samples were then removed and weighed to constant weight using the Gram-Atic balance. The water content was determined by taking the difference between the initial and the final weighing.

TABLE VII

DETERMINATION OF THE WATER CONTENT
IN MONAZITE

Sample #	Weight Of Wet Sample	Weight Of Dry Sample	Weight Of H_2O	$\%H_2O$ In Sample
7	0.8980 g	0.8968 g	0.0012 g	0.13%
8	0.9790 g	0.9776 g	0.0014 g	0.14%

PREPARATION OF RESIN AND ION-EXCHANGE COLUMN

The resin used was Amberlite CG-120. It was obtained from Mallinckrodt Chemical Works in New York. The resin is of chromatographic grade and is 100-200 mesh. It is a strongly acidic cation exchange resin of the sulfonated polystyrene type. The resin was put into a 1 liter beaker and washed with distilled water to remove the "fines". Three or four washings were necessary to complete the process. The maximum percentage of iron in the resin is 0.020%. To remove all iron which may be present the resin was heated on a water bath with 3M hydrochloric acid for two hours. After the acid was allowed to cool it was decanted and the acid washing was repeated three more times. After this process was complete the resin was washed several times with distilled water to remove all traces of hydrochloric acid. At this point the resin was stored in a 1 liter beaker until the ion-exchange column apparatus was properly assembled. The beaker was placed in a cool, shaded area so that the resin would remain in a moist condition.

The ion-exchange tube was obtained from Fisher Scientific Company. The tube was constructed of Pyrex glass which was constricted at the lower end. The length of the column was 400 mm with an inside diameter of 20 mm.

The ion-exchange resin was supported on a sealed-in coarse porosity fritted glass disk. The flow rate of the packed column was 50± 10 ml/hour.

INVESTIGATION AND PREPARATION OF THE ELUTING REAGENTS

K. S. Chung and J. P. Riley (14) carried out numerous experiments to determine the most satisfactory eluants for the separation of the rare-earth group from the other elements likely to be present in the sulphuric acid digest. Since monazite consists of metal phosphates it was decided to wash the column with distilled water until the eluate gave no reaction for phosphate. It was found that with 1 g samples, 2 l of distilled water were necessary. Further investigations by these authors found that with 2 l of 1 N hydrochloric acid, calcium, magnesium, manganese, lead, aluminum, iron, tin, titanium, uranium, sodium and potassium were completely eluted from the column.

TABLE VIII

ELUTION FROM THE COLUMN WITH 8 x 250 ml PORTIONS OF 1N HCl (14)

Element	Oxide taken (mg)	Weight (mg) of Element (as oxide) in Eluate									
		1	2	3	4	5	6	7	8	Total	% Recovery
Calcium	25.0	0.00	0.00	0.00	4.48	15.68	4.41	0.35	0.00	24.92	99.6
Magnesium	25.0	0.00	18.59	6.36	0.10	0.00	0.00	0.00	0.00	25.05	100.2
Manganese	5.0	2.47	2.54	0.01	0.00	0.00	0.00	0.00	0.00	5.02	100.4
Lead	20.0	18.93	1.02	0.00	0.00	0.00	0.00	0.00	0.00	19.95	99.8
Aluminum	15.0	0.00	0.00	0.00	1.30	12.40	1.40	0.10	0.00	15.20	101.3
Iron	17.21	0.289	7.06	9.10	0.62	0.13	0.01	0.00	0.00	17.21	99.9
Tin	107.6	105.6	2.4	0.00	0.00	0.00	0.00	0.00	0.00	108.0	100.4
Uranium	20.0	19.60	0.50	0.00	0.00	0.00	0.00	0.00	0.00	20.1	100.5
Titanium	8.0	———	———	7.96	———	———	———	0.00	0.00	7.96	99.5
Sodium	50.0	———	49.5	———	0.50	0.00	0.00	0.00	0.00	50.0	100.0
Potassium	20.0	———	20.0	———	0.00	0.00	0.00	0.00	0.00	20.0	100.0
Ytterbium	324.3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0
Praseodymium	298.9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0
Yttrium	342.8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0
Thorium	100.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0

The rare-earth group and thorium were not eluted with 1N hydrochloric acid. Further investigation showed that the rare-earth group was completely eluted from the column with 750 ml of 3N hydrochloric acid. The thorium remains on the exchange resin and may be removed with 800 ml of 3.6N sulphuric acid.

The 1N hydrochloric acid solution was prepared by diluting 366 ml of concentrated reagent grade hydrochloric acid to 2 l with distilled water. The 3N hydrochloric acid solution was prepared by diluting 1098 ml of concentrated reagent grade hydrochloric acid to 2 l with distilled water. The acid solution was titrated with sodium hydroxide to a phenolphthalein end point. The exact normalities of the acid was found to be 1.02N and 2.99N respectively.

The 400 ml solution of the sulphuric acid digest was passed through the column. The column was then washed with 3 l of distilled water to remove any traces of phosphate which could interfere with any of the determinations. The percolate and the washings were then rejected. All the metals less the rare-earth group and thorium were then removed by eluting the ion-exchange column with 2 l of 1.02N hydrochloric acid. This solution was also rejected as it was only the separation and determination of the rare-earth group which was of primary interest. The rare-earth group

was eluted from the column with 750 ml of 2.99N hydrochloric acid. The eluate was then divided up and placed in four 250 ml Vycor beakers and evaporated almost to dryness on a water bath. The residue was then twice evaporated to dryness with 10 ml portions of reagent grade concentrated nitric acid to remove the chlorides. The residue was taken up in 25 ml of 8.5 nitric acid which was diluted from reagent grade concentrated nitric acid, which was prepared by taking 13.9 ml of the concentrated nitric acid and diluting it to 25 ml with distilled water. This solution was then used to separate cerium from the other rare-earth elements. Cerium is not readily determined spectrophotometrically as it interferes with all other determinations in the lower region of the spectrum. The molar absorptivity of cerium also varies with temperature and cerium is difficultly soluble in one molar perchloric acid (4).

SEPARATION OF CERIUM FROM THE OTHER RARE-EARTH ELEMENTS

Most analytical methods of separating cerium is based on the fact that cerium is the only rare-earth which is easily oxidized from the trivalent state to the tetravalent state. Further, it is found that the properties of cerium (IV) compounds are different from those of the trivalent rare-earth group. Tetravalent cerium is easily extracted from a nitric acid medium by a number of organic

solvents. Diethyl ether has been used to extract cerium from the other rare-earths. The distinct disadvantages of using this solvent is that it has a tendency to creep and if any peroxide were present in the ether it would reduce the cerium back to the trivalent state. Glendenin et al. (21) studied the extraction of cerium with methyl isobutyl ketone and found cerium to be quantitatively extracted from 8-9N nitric acid. Methyl isobutyl ketone has several advantages over diethyl ether since it does not peroxidize, it is much less volatile and it does not creep like the ether.

The solution of the rare-earth elements in 25 ml of 8.5N nitric acid was transferred to a 250 ml separatory funnel using a further 25 ml of 8.5N nitric acid. A Cent-O-Gram triple beam balance was used to weigh out 0.5 g of Fisher Certified Reagent Grade sodium bromate. This was used to oxidize the cerium from the trivalent state to the tetravalent state. The rare-earth mixture was then extracted with 100 ml of Fisher Certified Reagent Grade methyl isobutyl ketone for three minutes. The organic phase was then poured via the top of the separatory funnel into a 250 ml separatory funnel containing 25 ml of 8.5N nitric acid. After shaking for two minutes the ketone phase was transferred to a 500 ml separatory funnel containing 100 ml of distilled water and 1 ml of 30% Fisher Certified Reagent

Grade hydrogen peroxide. The first nitric acid phase is re-extracted with a further 100 ml of methyl isobutyl ketone followed by four extractions with 50 ml of the ketone. In each case the extract was washed with the 25 ml aliquot of 8.5N nitric acid to remove any extracted rare-earth elements. The two nitric acid phases were then quantitatively transferred to a 600 ml beaker and evaporated to dryness on a water bath. This residue was then used to determine the rare-earth elements less cerium.

The 500 ml separatory funnel containing the combined methyl isobutyl ketone extracts and dilute hydrogen peroxide was shaken for two minutes to transfer the cerium to the aqueous phase. The aqueous phase was run into a 500 ml beaker and the ketone phase was washed three times with distilled water to remove any entrained cerium. The aqueous phase and the washings were then evaporated to dryness on a water bath. This residue was used for the quantitative determination of cerium.

QUANTITATIVE DETERMINATION OF CERIUM

The residue from the evaporation of cerium was dissolved in 450 ml of distilled water to which 2 ml of reagent grade concentrated nitric acid was added. Thirty ml of a saturated oxalic acid solution was added with constant stirring. The solution was heated on a Thermolyne

hot plate to 68°C. The pH of the solution was adjusted with reagent grade concentrated ammonium hydroxide until the solution was just on the acid side. The beaker was then covered with a watch glass and allowed to digest for 24 hours. On the following day, the solution was filtered without suction through 11.0 cm diameter Whatman No. 541 filter folded within a No. 42 filter. The precipitate was transferred to the filter with a jet of hot distilled water. The precipitate and the filter were then washed with hot distilled water and transferred to a weighed platinum crucible. The crucible was gently heated using a bunsen burner until all moisture and most of the paper was burned off. The platinum crucible was then placed in a muffle furnace at 900°C until all the carbon was burned off. The crucible was then heated to 1000°C for 1 hour, cooled in a dessicator and weighed as the dioxide.

TABLE IX

DETERMINATION OF CERIUM IN THE SAMPLE

Sample #	Weight Of Sample	Weight CeO_2	% $CePO_4$
5	1.1390 g	.4300 g	43.4
6	1.3281 g	.4990 g	43.3

THE DETERMINATION OF THE RARE-EARTH ELEMENTS LESS CERIUM AND ELEMENTS ASSOCIATED WITH THE RARE-EARTH ELEMENTS

The residue from the nitric acid evaporation was dissolved in 450 ml of distilled water to which 2 ml of reagent grade concentrated nitric acid was added. Thirty ml of a saturated oxalic acid solution was added with constant stirring. The solution was heated on a Thermolyne hot plate to 68°C. The pH of the solution was adjusted with reagent grade concentrated ammonium hydroxide until the solution was slightly acidic. The beaker was then covered with a watch glass and allowed to digest for 24 hours. On the following day, the solution was filtered without suction through 11.0 cm diameter Whatman No. 541 filter folded within a No. 42 filter. The precipitate was transferred to the filter with a jet of hot distilled water. The precipitate and the filter were then washed with hot distilled water and transferred to a platinum crucible. The crucible was gently heated with a bunsen burner until all moisture and most of the paper was burned off. The platinum crucible was then placed in a muffle furnace at 900°C until all the carbon was burned off. The crucible was then heated to 1000°C for 1 hour, cooled

in a dissicator and stored as the oxide.

The oxide was then transferred quantitatively to a 250 ml round bottom flask using 10 ml of 60% Reagent Grade perchloric acid. Forty additional ml of perchloric acid were added and the solution was refluxed using a ground glass reflux condenser for two hours. At the end of this time a clear solution was obtained. The solution was then transferred to a 1 l volumetric flask using 100 ml of distilled water. The solution was then diluted to 1 l.

SPECTROPHOTOMETRIC EVIDENCE OBTAINED WITH THE MODEL D U SPECTROPHOTOMETER

The Beckman Model D. U. Spectrophotometer was chosen to investigate the absorption spectra of the rare-earth elements from 425mμ to 750mμ. The slit width was set at 0.5 mm, from 425mμ to 625mμ the photomultiplier attachment was used and from 625mμ to 750mμ the red sensitive phototube was employed. The sensitivity control was set at 3. The 22 megohm resister was used with the photomultiplier and the 2,000 megohm resister was used with the red sensitive phototube. The sample was pipetted into one Beckman Rectangular Cell and dilute perchloric acid was placed in the other cell as a blank. An investigation of the region from 425mμ to 750mμ showed that no absorption bands were present indicating the absence of the rare-earth group except cerium, lanthanum and possibly

yttrium which have no absorption in this region of the spectrum.

ANALYSIS OF A KNOWN SAMPLE CONTAINING SEVERAL MEMBERS OF THE RARE-EARTH GROUP

Since the rare-earth elements could not be detected by absorption in the 425 mμ to 750 mμ region of the spectrum, a known sample was run to make sure the rare-earth elements were not being lost due to an analytical error. A known sample was prepared containing .1577 g samarium, .2539 g neodymium and .3283 g praseodymium. To this was added 2.2406 g ammonium phosphate so as to have the known sample resemble a typical monazite sample where they would all be present as the phosphates. This sample was then run through the exact analysis which was presented previously; this included the same period of digestion; same ion-exchange column conditions including the same solutions; extraction with methyl isobutyl ketone; precipitation with oxalic acid and the burning of the sample to the oxide. The oxide was then transferred to a 250 ml round bottom flask and refluxed with 50 ml of 60% perchloric acid for two hours. It was then quantitatively transferred to a 1 l volumetric flask and diluted to 1 l. Using the same techniques and duplicating conditions wherever possible the solution was analyzed with the Beckman Model D. U. Spectrophotometer. Since samarium absorbs at 401.6 mμ, neodymium at 575.5 mμ

and praseodymium at 444.0 mμ it was decided to investigate these three regions of the spectrum. Samarium, neodymium and praseodymium were obtained as the oxalates (99.9%), and burned @ 1000° for two hours to the oxides.

TABLE X

AN INVESTIGATION OF THE 390 mμ TO 410 mμ REGION OF THE SPECTRUM FOR THE DETERMINATION OF SAMARIUM

mμ	A	mμ	A
390	.105	408	.120
391	.108	409	.125
392	.107	410	.117
393	.107		
394	.110		
395	.115		
396	.122		
397	.130		
398	.142		
399	.176		
400	.220		
401	.257		
402	.250		
403	.200		
404	.155		
405	.127		
406	.130		
407	.130		

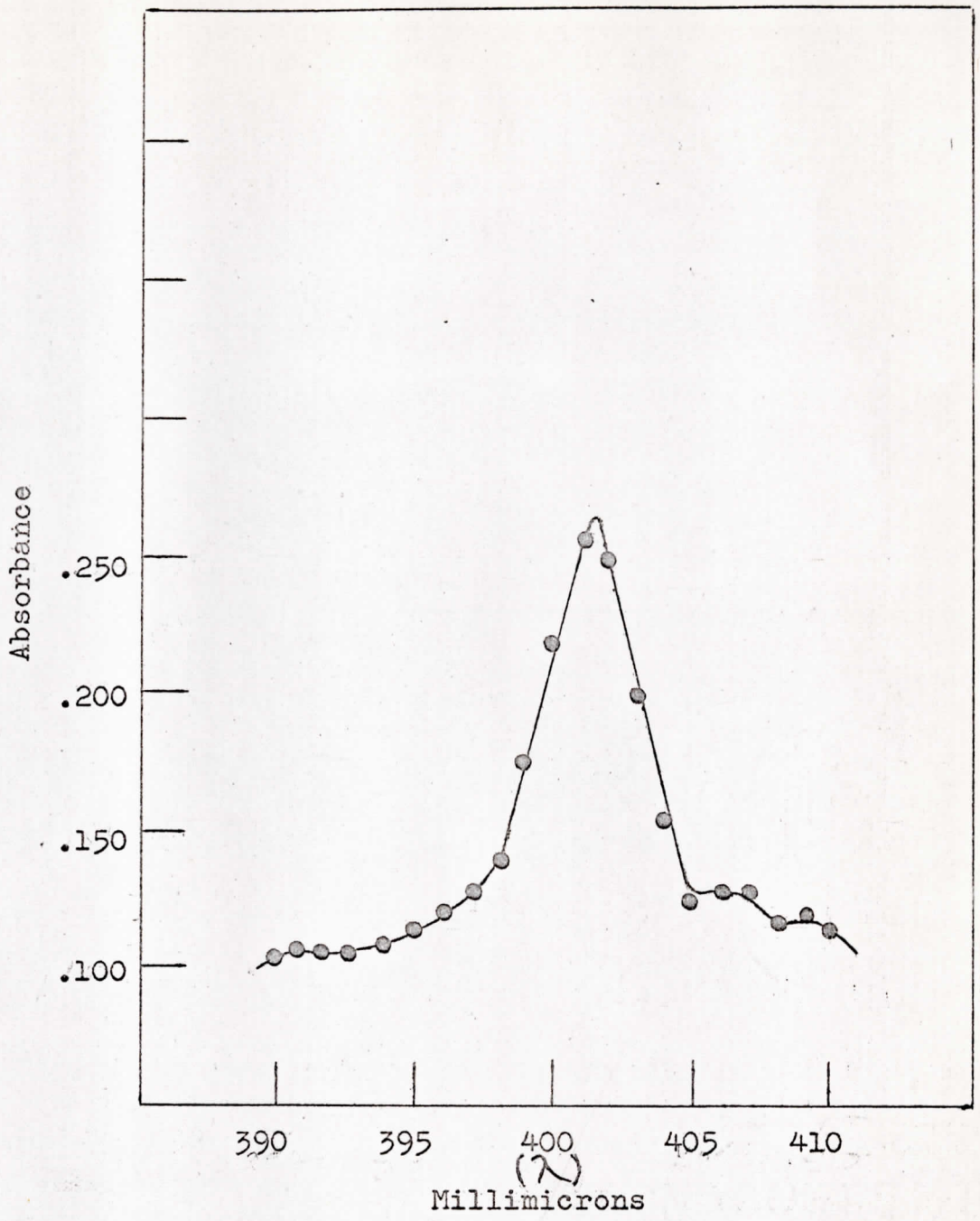

FIGURE I

ABSORPTION SPECTRA OF SAMARIUM

TABLE XI

AN INVESTIGATION OF THE 435mμ TO 455mμ REGION OF THE SPECTRUM FOR THE DETERMINATION OF PRASEODYMIUM

mμ	A
435	.123
436	.128
437	.128
438	.145
439	.163
440	.189
441	.215
442	.253
443	.289
444	.285
445	.257
446	.215
447	.180
448	.165
449	.153
450	.146
451	.138
452	.138
453	.139
454	.140
455	.143

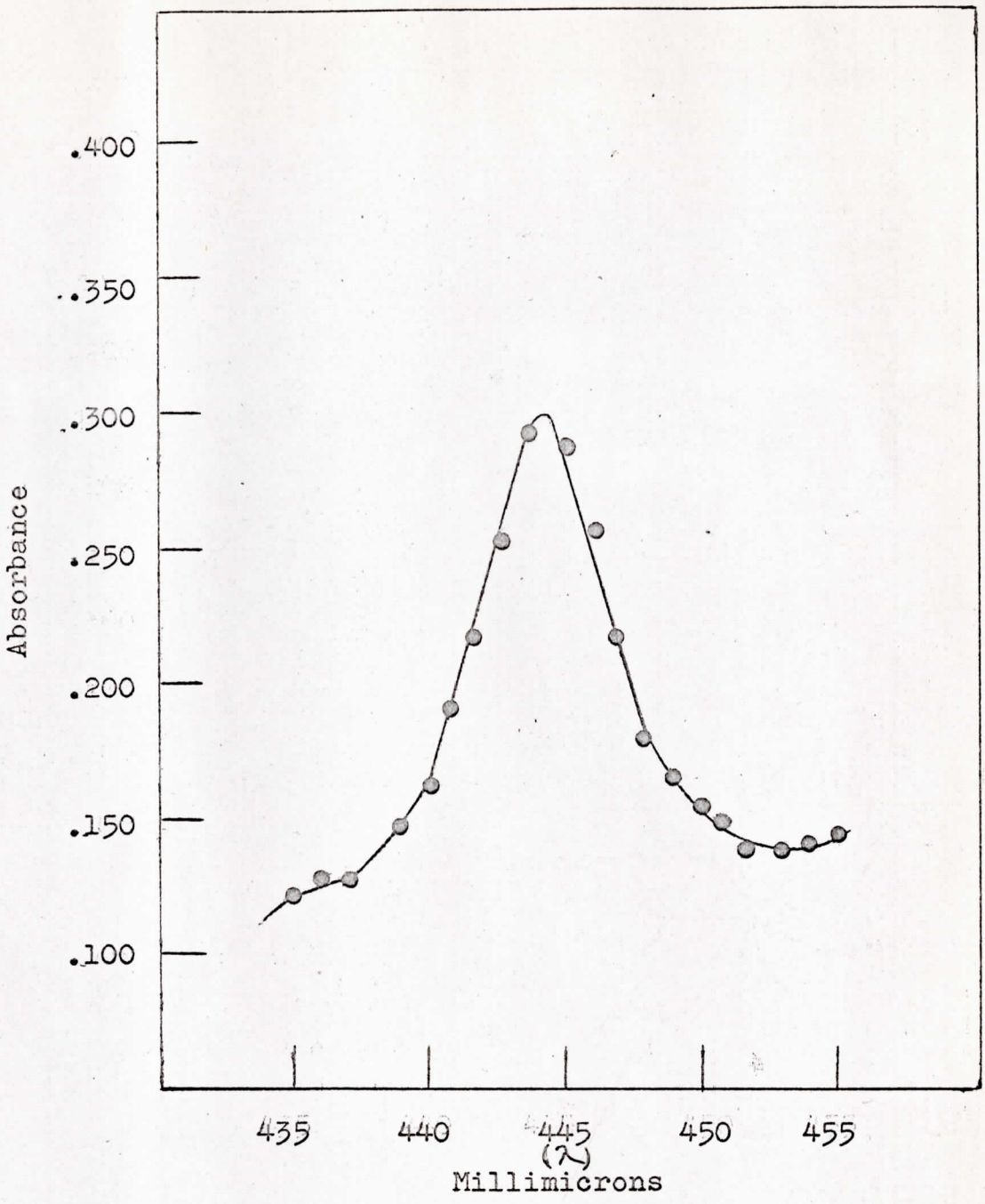

FIGURE II

ABSORPTION SPECTRA OF PRASEODYMIUM

TABLE XII

AN INVESTIGATION OF THE 565 mμ TO 585 mμ REGION OF THE SPECTRUM FOR THE DETERMINATION OF NEODYMIUM

mμ	A
565	.133
566	.145
567	.165
568	.200
569	.258
570	.352
571	.428
572	.465
573	.535
574	.562
575	.560
576	.540
577	.475
578	.422
579	.353
580	.312
581	.285
582	.250
583	.235
584	.207
585	.140

SPECTROPHOTOMETRIC EVIDENCE OBTAINED WITH THE BECKMAN MODEL B SPECTROPHOTOMETER WITH THE FLAME ATTACHMENT

Since no absorption spectra of the rare-earth group could be obtained, it was decided to investigate the emission spectra as a means for a qualitative and a quantitative analysis. The instrument utilized was the Beckman Model B Spectrophotometer with the Beckman 9125 Flame Attachment. The attachment consists of an acoustically-insulated burner housing, a control panel for precise regulation of fuel and oxygen pressures, and a base assembly for assuring proper alignment of the components. The only additional items required are the tanks of oxygen and acetylene fitted with regulators and gages. (20) The blue sensitive phototube was employed, the sensitivity control was set at 4, and the slits were opened to 1 mm. The tank of oxygen was opened to 50 psi. and the tank of acetylene was opened to 10 psi. The oxygen on the control panel was slowly increased to 13.5 psi. and the acetylene was slowly increased to 2.5 psi. The solution which was utilized for the absorption spectral analysis was used for the emission analysis. Again a dilute solution of 60% perchloric acid was used as a blank during the analysis.

TABLE XIII

AN INVESTIGATION OF THE EMISSION SPECTRA OF THE RARE-EARTH GROUP IN THE 400 mμ TO 600 mμ REGION OF THE SPECTRUM

mμ	% T	mμ	% T
400	0.0	500	20.0
405	0.0	505	22.5
410	0.0	510	22.0
415	0.0	515	24.0
420	4.1	520	26.0
425	5.0	525	27.0
430	10.5	530	33.0
435	29.9	535	38.0
440	48.0	540	45.0
445	40.0	545	54.5
450	25.3	550	60.0
455	18.0	555	64.0
460	19.5	560	64.0
465	19.5	565	62.5
470	19.0	570	60.0
475	19.2	575	56.0
480	20.0	580	52.5
485	22.0	585	52.0
490	23.2	590	52.5
495	20.0	595	49.0
		600	44.0

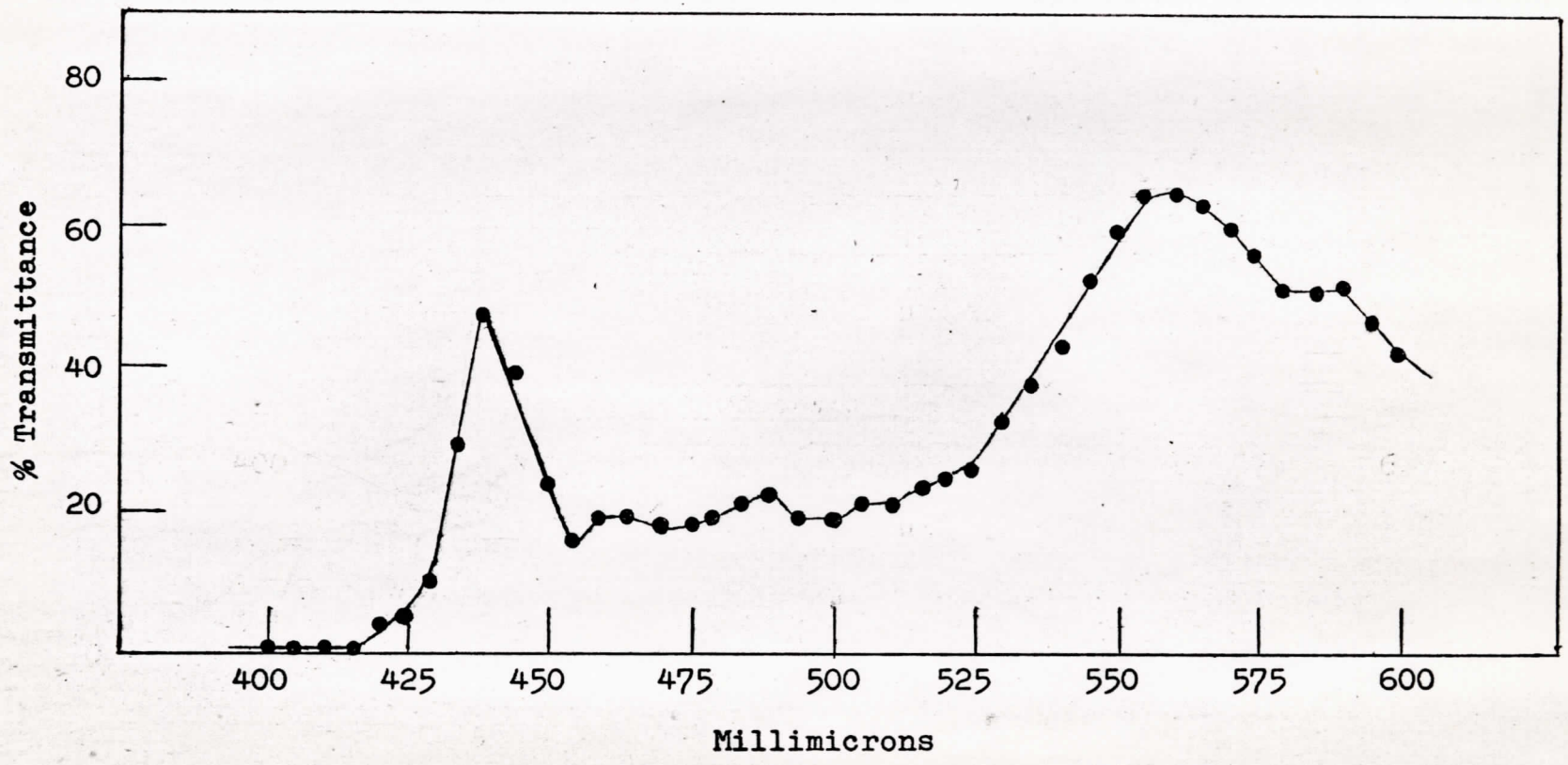

FIGURE IV

A SCAN OF THE EMISSION SPECTRA
OF THE MONAZITE SAMPLE FROM
400mμ TO 600mμ

The emission peaks at 440mμ and 560 mμ corresponded to the emission peaks reported in the literature for lanthanum. A small peak at about 490mμ was further investigated using a photomultiplier and narrowing the slits. The reason for interest in this peak was due to the fact that an emission peak for yttrium is listed at 483mμ . The region from 475mμ to 490 mμ was carefully investigated with the sensitivity set at 4, the slits opened to 0.1 mm, and the photomultiplier dial set at the D position. The oxygen and acetylene pressures were 50 psi. and 10 psi. respectively on the tanks and 13.5 psi. and 2.5 psi. respectively on the control panel.

TABLE XIV

AN INVESTIGATION OF THE EMISSION SPECTRA
IN THE 475 mμ TO 490 mμ REGION OF THE SPECTRUM

mμ	% T	mμ	% T
475	13.2	483	22.0
476	13.1	484	20.8
477	13.1	485	19.0
478	13.1	486	17.0
479	13.0	487	17.0
480	14.5	488	15.8
481	18.3	489	15.5
482	20.2	490	14.8

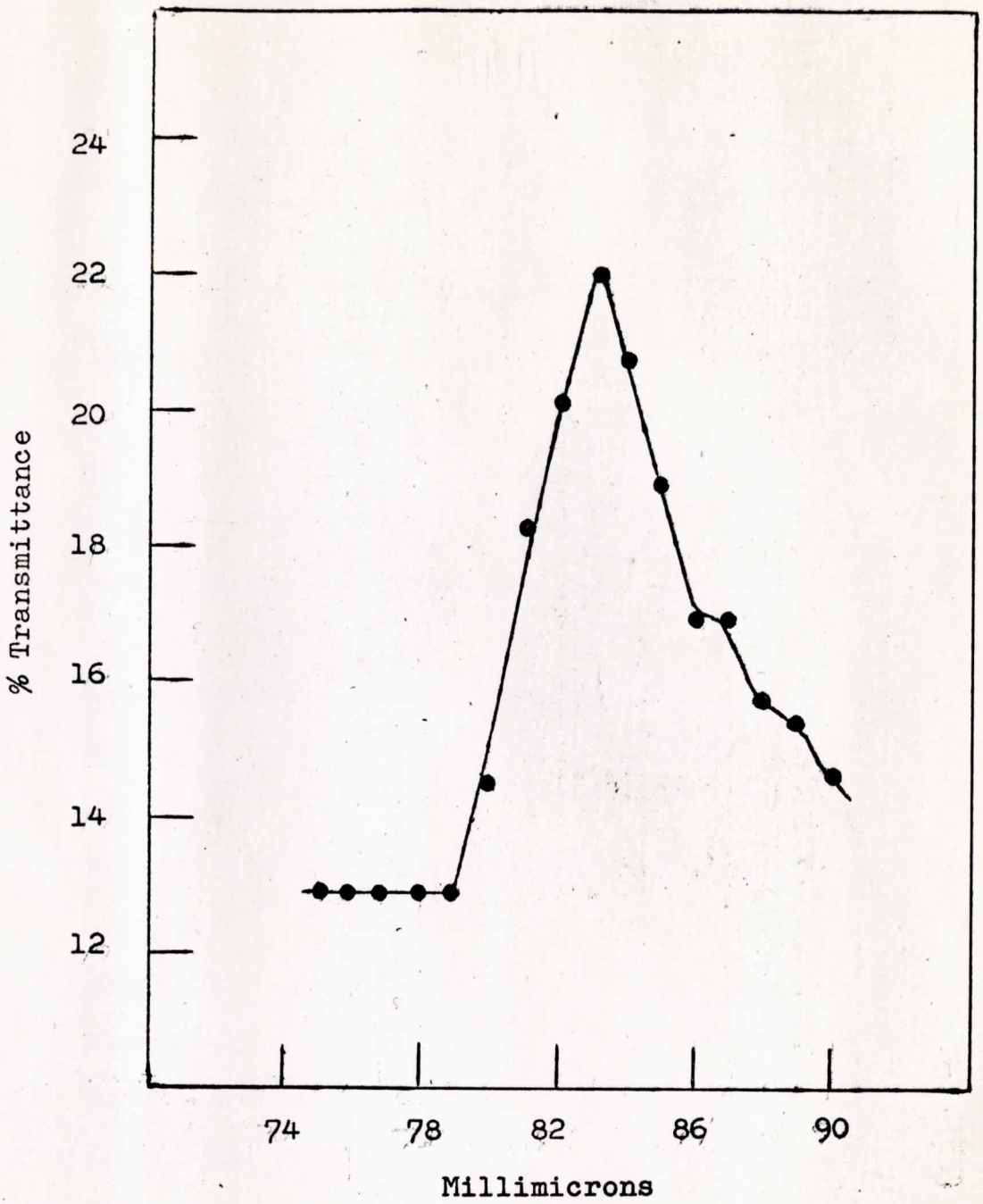

FIGURE V

A SCAN OF THE EMISSION SPECTRA
OF THE MONAZITE SAMPLE FROM
475 mμ To 490 mμ

QUANTITATIVE DETERMINATION OF LANTHANUM

Since lanthanum emits a strong sharp peak at 440 mμ it was decided to use this peak for the quantitative determination of lanthanum. Using the peak at 440 mμ ten standard solutions were prepared and a calibration curve was constructed. The ten solutions were prepared by dissolving 1.6473 g of lanthanum oxide in 50 ml of 60% reagent grade perchloric acid. The perchloric acid was then refluxed, and after all the oxide dissolved the solution was quantitatively transferred to a 1 l volumetric flask and diluted to 1 l. Ten solutions were then prepared by withdrawing different aliquots and diluting each aliquot to 50 ml with distilled water in a 50 ml volumetric flask. The slits on the Model B were set at 0.2 mm, the sensitivity was set at 4 and a photomultiplier was used with the dial set in the D position. The tanks of oxygen and acetylene were opened to 50 psi. and 10 psi respectively. The gases on the control panel were adjusted to 13.5 psi. for oxygen and 2.5 psi. for the acetylene.

TABLE XV

STANDARD SOLUTIONS OF La_2O_3

ml La_2O_3	ml H_2O	ppm of La
50	0	1404.5
40	10	1123.6
35	15	983.1
30	20	842.7
20	30	561.8
15	35	421.4
10	40	280.9
5	45	140.5
3	47	84.3
1	49	28.1

TABLE XVI

CONCENTRATION OF LANTHANUM Vs
% TRANSMITTANCE

Parts Per Million Lanthanum	% Transmittance
1404.5	93.0
1123.6	83.0
983.1	77.0
842.7	71.0
561.8	59.8
421.4	55.0
280.9	49.5
140.5	44.0
84.3	43.0
28.1	41.0

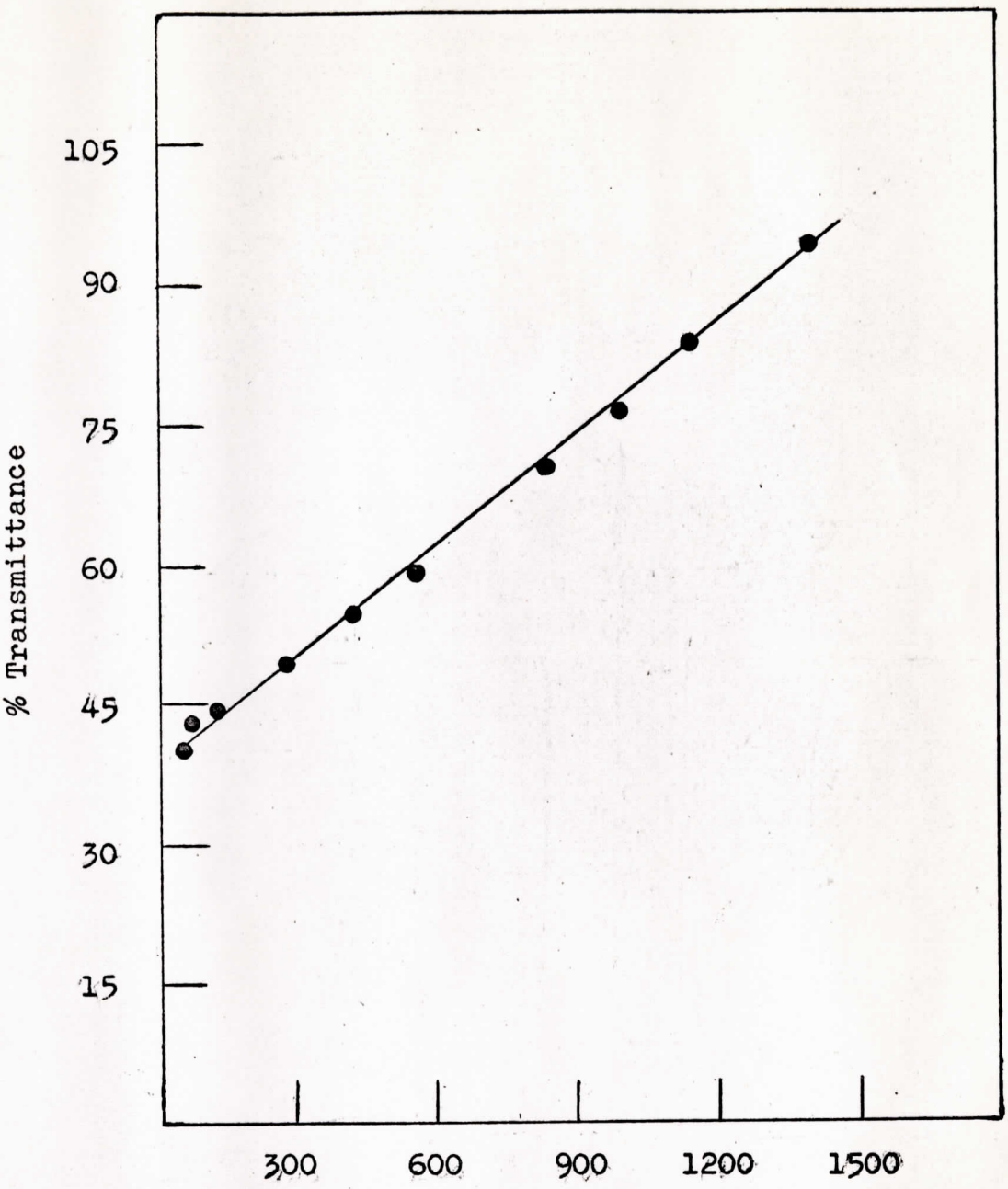

FIGURE VI

CALIBRATION CURVE FOR LANTHANUM

TABLE XVII

QUANTITATIVE DETERMINATION OF LANTHANUM

Sample #	Weight Of Sample	% T	ppm La	% $LaPO_4$
5	1.1390 g	48.0	260 ppm	37.4%
6	1.3281 g	50.0	300 ppm	36.9%

QUANTITATIVE DETERMINATION OF YTTRIUM

The emission peak at 483 mμ was used for the quantitative determination of yttrium. Six standard solutions were prepared and a calibration curve was constructed. The six standard solutions were prepared by dissolving .2214 g of dried 99.99% yttrium oxide in 50 ml of 60% reagent grade perchloric acid. The perchloric acid solution was refluxed, and after all the oxide dissolved, the solution was quantitatively transferred to a 1 l volumetric flask and diluted to 1 l. The six solutions were then prepared by diluting the standard solution with the appropriate amount of distilled water. The slits on the Model B were set at 0.2 mm, the sensitivity was set at 4 and a photomultiplier was used with the dial set in the D position. The tanks of oxygen and acetylene were regulated in exactly the same way as was done in the lanthanum determination.

TABLE XVIII

STANDARD SOLUTIONS OF Y_2O_3

ml Y_2O_3	ml H_2O	ppm Y
50	0	174.4
40	10	137.5
30	20	104.6
20	30	67.8
15	35	52.3
10	40	34.9

TABLE XIX

CONCENTRATION OF YTTRIUM Vs
% TRANSMITTANCE

Parts Per Million Yttrium	% Transmittance
174.4	10.3
137.5	7.8
104.6	5.6
67.8	3.0
52.3	2.0
34.9	1.0

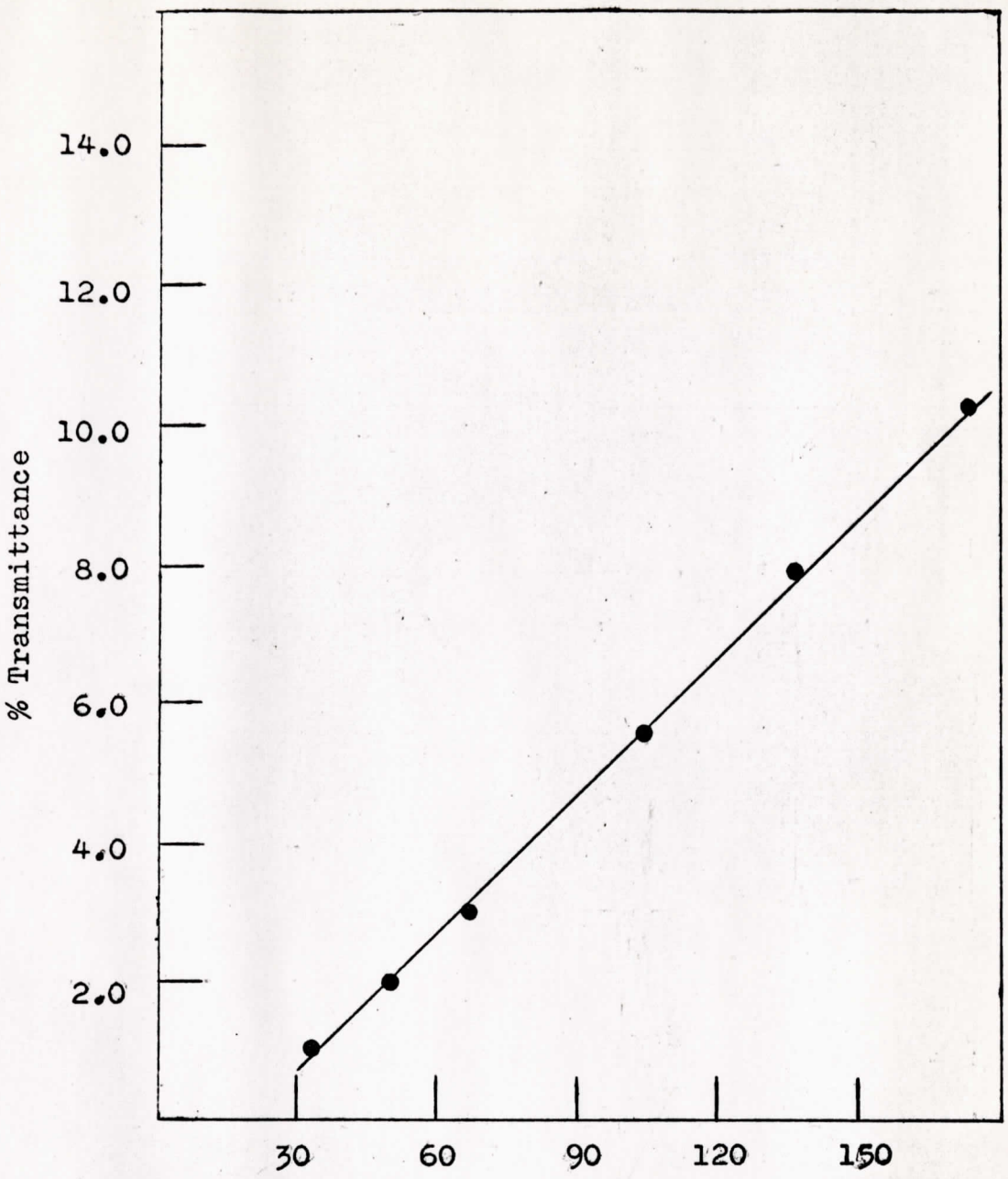

FIGURE VII

CALIBRATION CURVE FOR YTTRIUM

TABLE XX

QUANTITATIVE DETERMINATION OF YTTRIUM

Sample #	Weight Of Sample	% T	ppm Y	% YPO_4
5	1.1390 g	2.4	57.0	10.4
6	1.3281 g	3.0	66.0	10.3

CHAPTER IV

SUMMARY AND CONCLUSIONS

SUMMARY

A sample of monazite, a thorium-rare-earth phosphate which was obtained from Madison County, North Carolina was analyzed for rare-earths and metals associated with the rare-earths. Two samples were taken through the complete analysis for the rare-earth metals. In addition to the rare-earth metal content, the percent moisture and percent insoluble residue was also calculated.

An ion-exchange column was set up using Amberlite CG 120 as the resin. The rare-earth metals were washed from the column using 750 ml of 2.99N hydrochloric acid. The metals were then evaporated and taken back up as the nitrates. Cerium was separated from the other metals by liquid-liquid extraction techniques using a solvent of methyl-isobutyl ketone. The cerium was quantitatively determined by precipitation with oxalic acid and burning the precipitate in a muffle furnace at 1000°C to obtain the oxide. The other rare-earth metals were also precipitated as the oxalates and burned to the oxides. The only other metals observed were lanthanum and yttrium which were quantitatively determined using the Beckman 9125 Flame Attachment with the Model B Spectrophotometer.

CONCLUSIONS

The two samples of monazite which were analyzed contained 43.4% and 43.3% of cerium phosphate, 37.4% and 36.9% of lanthanum phosphate, 10.4% and 10.3% of yttrium phosphate. It was interesting to find that no rare-earth other than cerium was found. Experimental evidence based on emission and absorption spectra indicates that not even trace amounts of the other rare-earth elements were present. The water and ash content is in agreement with other published results, as is the cerium, lanthanum and yttrium which was found in the monazite sample.

TABLE XXI

ANALYSIS OF THE MONAZITE SAMPLE

Sample #	% Insoluble Residue	% Moisture	% $CePO_4$	% $LaPO_4$	% YPO_4
5	8.42		43.4	37.4	10.4
6	8.41		43.3	36.9	10.3
7		.13			
8		.14			

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